

The forming process of authigenic pyrite and gypsum in core sediment from the northern South China Sea and the implications to methane seepage intensities

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The northern slope of South China Sea is a gas hydrate-bearing region, related to high deposition rates of organic-rich sediments co-occurring with intense methanogenesis in the subsurface environment. Anaerobic oxidation of methane (AOM) coupled with bacterial sulfate reduction result in the precipitation of solid phase minerals including pyrite and gypsum in seepage sediment. Abundant aggregates of pyrites and gypsums were observed between the depth of 580cm and 810cm below the seafloor in the whole core sediment of HS328 from the northern South China Sea. Most of pyrites are tubes consisting of framboids and octahedrons. Gypsum aggregates occur as rosettes and spheroids consisting of plates. Some of them grew over pyrite, indicating that gypsum precipitation postdated pyrite formation. The $\delta^{34}\text{S}$ values of pyrite vary greatly (from -46.6‰ to -12.3‰ V-CDT) and increase from shallow to greater depth, which indicates the pyrite was resulted from bacterial reduction of sea-water sulfate driven by organic matter in the shallow sediments and was influenced by AOM with depth. The relatively higher abundance and $\delta^{34}\text{S}$ values of pyrite at the greater depth (580cm and 810cm) sediments indicates that this interval was the location of a paleo-sulfate methane transition zone (SMTZ). The sulfur isotopic compositions of gypsum fell within a narrow range (from -25‰ to -20.7‰) and are much lower than the sulfur isotopic composition of the seawater sulfate, indicating that the existence of a ^{34}S -depletion source of sulfur species which most likely are products of the oxidation of hydrogen sulfide or pyrite formed in organic matter driven sulfate reduction. These reactions lie to the circulation of oxygen-rich solutions by bioirrigation activity of benthic organisms. The $\delta^{34}\text{S}$ values of gypsum at greater depth are lower than those of the associated pyrite, revealing that ^{34}S -depleted sulfate downward diffusion to the greater depth. These sulfate lead to the increasing of Ca^{2+} ions from the dissolution of calcium carbonate mineral to supersaturated relative to gypsum in the pore solution. The higher abundance and characteristic sulfur isotopic composition of pyrite and gypsum may be taken as evidence of intense methane seepages.

Key words: Pyrite tube, Authigenic gypsum, Sulfur isotopes.